

Effect of Beta Low Irradiation Doses on the Micromechanical Properties of Surface Layer of LDPE

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Abstract. The experimental study deals with the effect of modification of the surface layer by irradiation cross-linking on the micromechanical properties of the low-density polyethylene (LDPE) tested using the instrumented nanohardness test. The surface layer of LDPE specimen made by injection technology was modified by irradiation cross-linking using beta irradiation, which significantly influences micromechanical properties of the surface layer. Compared to the heat and chemical-heat treatment of metal materials (e.g. hardening, nitridation, case hardening), cross-linking in polymers affects the surfaces in micro layers. These micromechanical changes of the surface layer are observed in the instrumented microhardness test. Our research confirms the comparable properties of surface layer of irradiated LDPE with highly efficient polymers. The subject of this research is the influence of irradiation dosage on the changes of micromechanical properties of surface layer of LDPE.

Introduction. Low-density polyethylene (LDPE) is a commodity polymer used extensively in extrusion operations such as coating, blown film, blow molding, and foaming. Extrusion of LDPE foams by direct gas injection or the so-called physical foaming can be separated in to five distinctive steps, i.e. melting of the solid LDPE pellets, injection and mixing of the liquid gas in the molten LDPE, cooling and shaping of the melt into the expansion condition, foaming of the melt by the expanding gas and finally cooling of the foam. Although viscosity and melting/crystallization behavior plays an important role in each or most of these process steps, the gas expansion is the crucial step in the foam process. In order to obtain a good foam quality (regular fine cell size and high closed cell content), the gas laden melt needs to be cooled down to a temperature close to the crystallization temperature of the semi-crystalline polyolefin to increase the melt viscosity and reduce the time needed for the transition from melt to solid phase. In practice, this means for semi-crystalline LDPE that the temperature of the melt at the die exit is always a few degree centigrade above the crystallization temperature [1-4].

Experimental

Materials. For this experiment High Density Polyethylene HDPE DOW – HDPE 25055E, DOW - Chemical company, USA (unfilled, HDPE) was used. The prepared specimens were irradiated with doses of 0, 33, 66 and 99 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 420C. Processing temperature 220–280 °C, mold temperature 70 °C, injection pressure 65 MPa, injection rate 45 mm/s.

Instrumented nanohardness tests were done using a Nanoindentation Tester (NHT2) – Opx/Cpx, CSM Instruments (Switzerland) according to the CSN EN ISO 14577-1. Load and unload speed was 20 mN/min. After a holding time of 90 s at maximum load 10 mN the specimens

were unloaded. The specimens were glued on metallic sample holders. Fifteen specimens were tested and average values are reported.

The indentation hardness H_{IT} was calculated as maximum load to the projected area of the hardness impression according to [3-7]:

$$H_{IT} = \frac{F_{max}}{A_p} \quad (1)$$

The indentation modulus is calculated from the Plane Strain modulus using an estimated sample Poisson's ratio:

$$E_{IT} = E^* \cdot (1 - \nu_s^2) \quad (2)$$

Determination of indentation creep C_{IT} (as can be seen at Fig. 1):

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \quad (3)$$

Where h_1 is the indentation depth at time t_1 of reaching the test force (which is kept constant), h_2 is the indentation depth at time t_2 of holding the constant test force [5-6].

Elastic part of the indentation work η_{IT} (as can be seen at Fig. 2):

$$\eta_{IT} = \frac{W_{elast}}{W_{total}} \cdot 100 \quad \text{with} \quad W_{total} = W_{elast} + W_{plast} \quad (4)$$

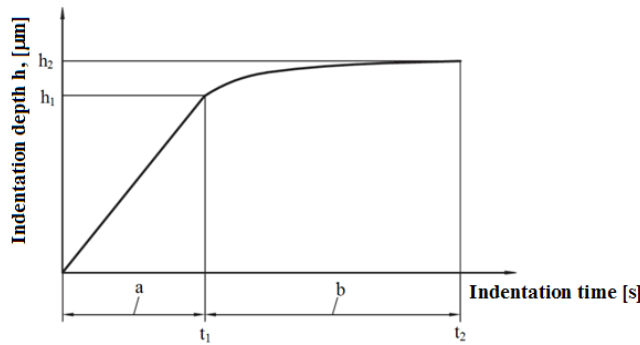


Fig. 1 Expression of indentation creep

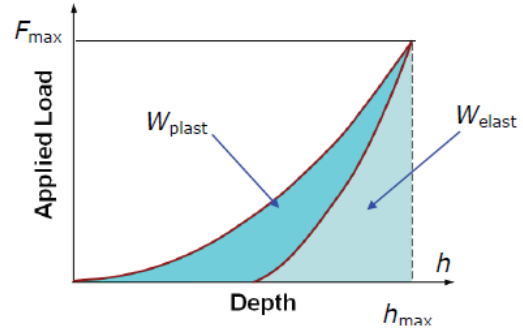


Fig. 2 Indentation work

Results and discussion

The values measured during the nanohardness test showed that the highest values of indentation hardness were found for the non-irradiated LDPE. On the contrary, the lowest values of indentation hardness were obtained for LDPE irradiated by a dose of 33 kGy (by 25% lower in comparison with the non-irradiated LDPE), as can be seen at Fig. 3.

Higher radiation dose does not influence significantly the nanohardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the nanohardness results reveals that when the highest radiation doses are used, nanohardness decreases which can be caused by radiation induced degradation of the material.

Radiation, which penetrated through specimens gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behavior.

According to the results of measurements of nanohardness, it was found that the lowest values of indentation modulus of elasticity were achieved at the LDPE irradiated with dose of 33 kGy (by 12% lower than compared with non-irradiated LDPE). On the contrary, the highest values of the indentation modulus of elasticity were found for non-irradiated LDPE as is seen at Fig. 4.

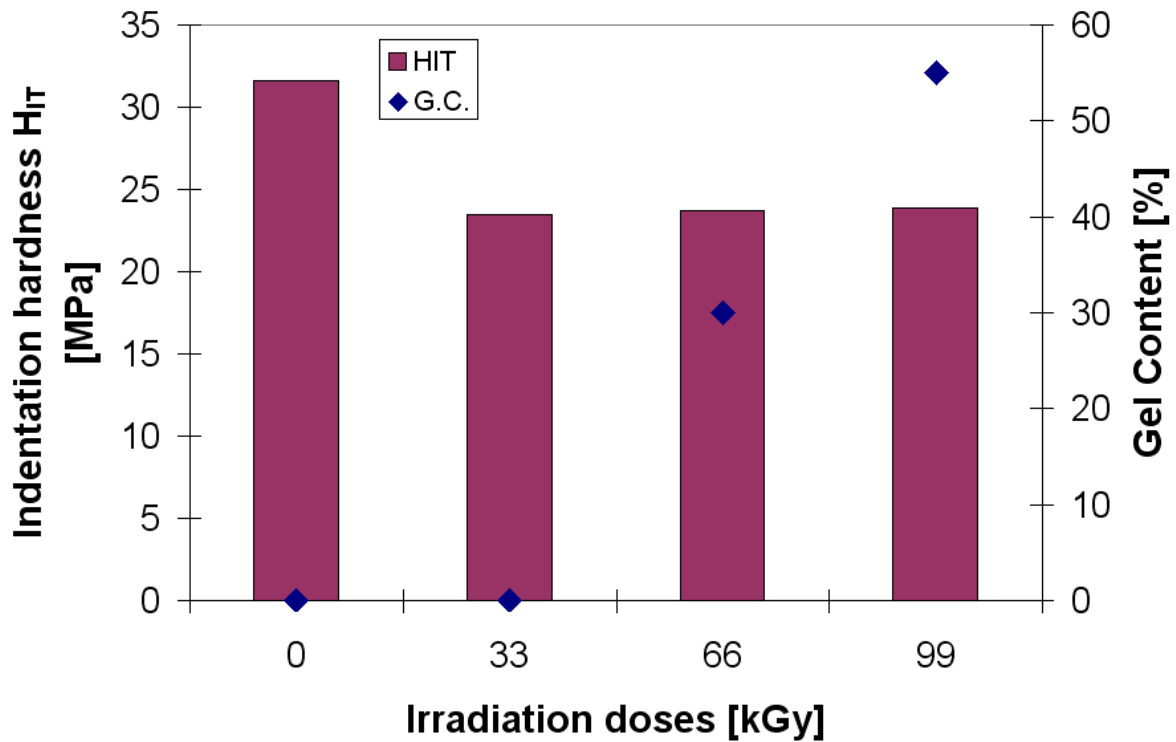


Fig. 3 Hardness H_{IT} vs. irradiation doses of LDPE

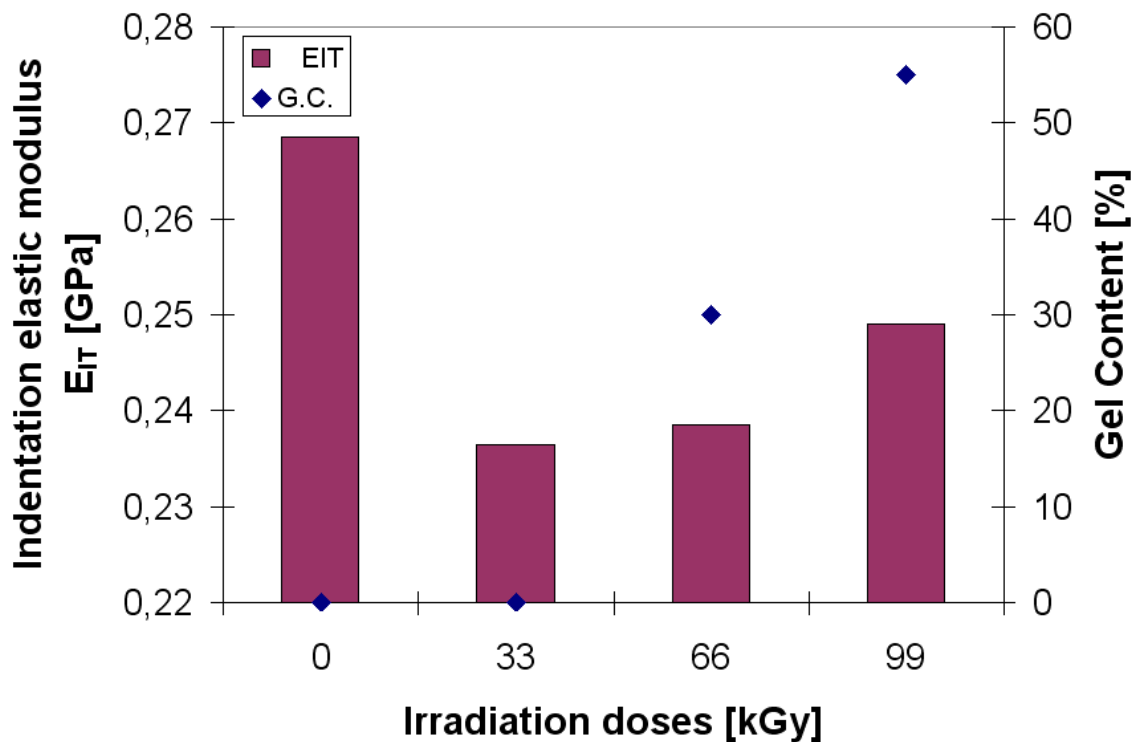


Fig. 4 Indentation modulus E_{IT} vs. irradiation doses of LDPE

According to the results of measurements of nanohardness, it was found that the highest values of indentation creep were achieved at the LDPE irradiated with dose of 33 kGy (by 31% lower than compared with non-irradiated LDPE). On the contrary, the highest values of the indentation creep were found for non-irradiated LDPE as is seen on Fig. 5.

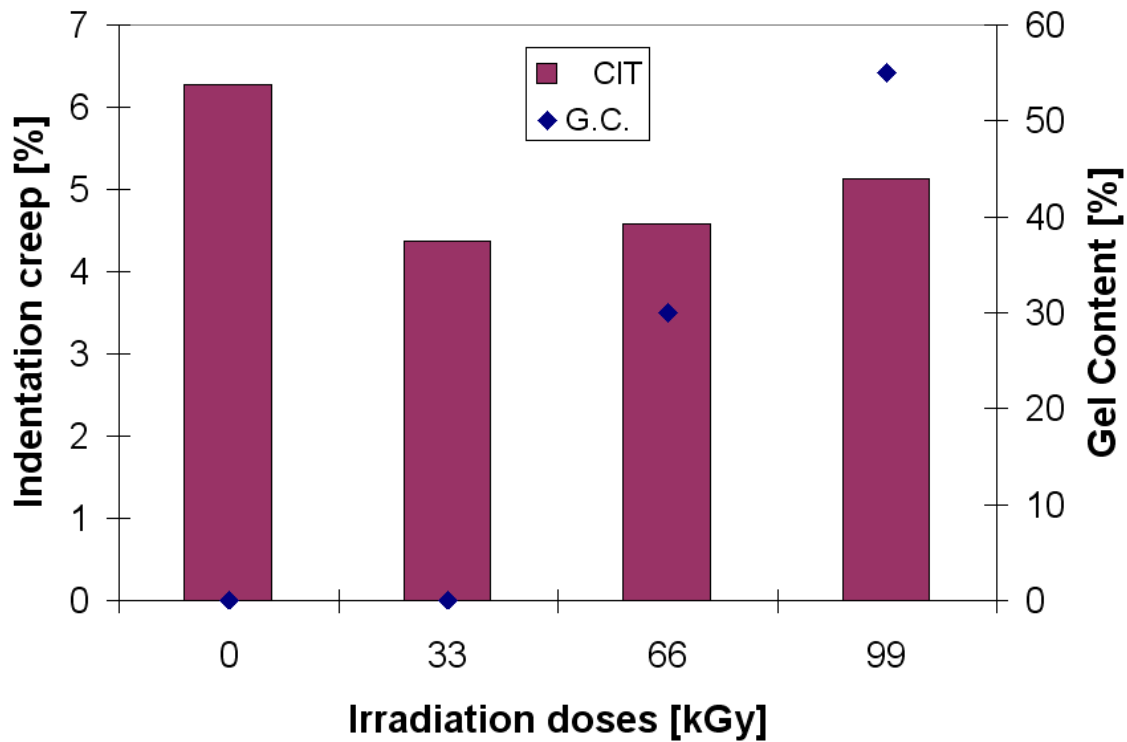


Fig. 5 Indentation creep C_{IT} vs. irradiation dose of LDPE

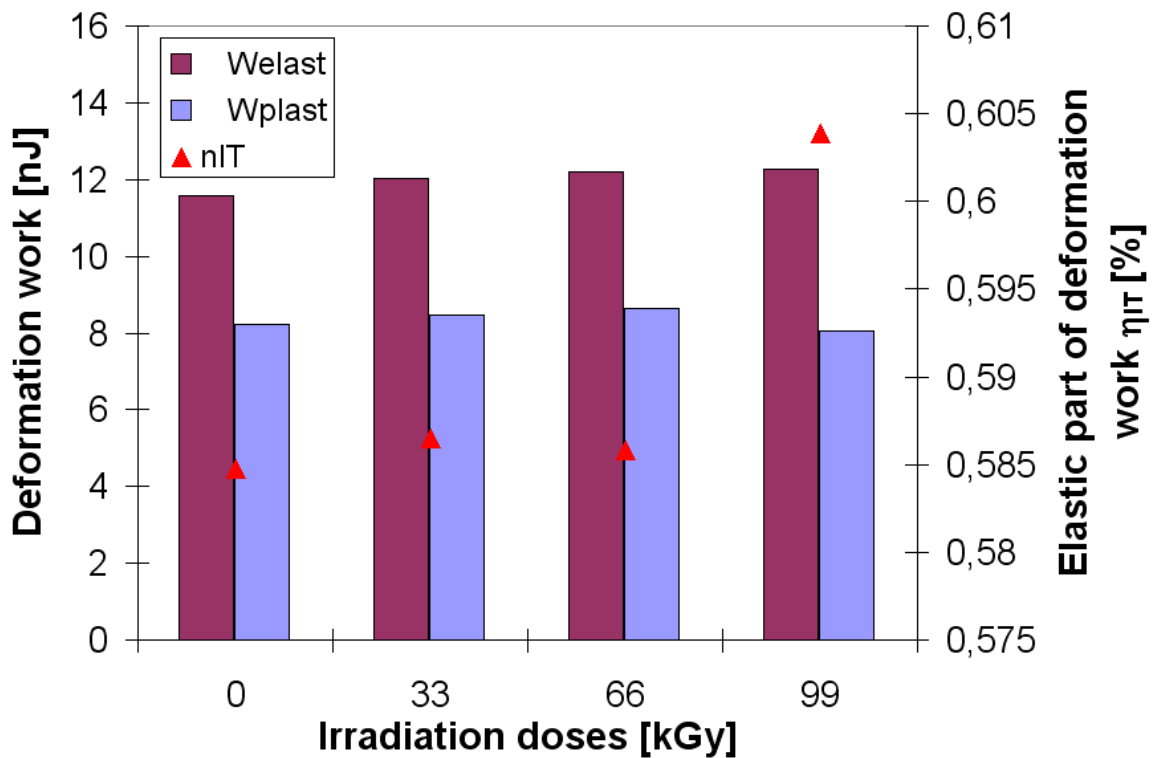


Fig. 6 Deformation work vs. irradiation dose of LDPE

Interesting results were found for elastic and deformation work. The lowest value of elastic work was measured for non-irradiated LDPE while the highest value of plastic deformation work was found at the radiation dose of 66 kGy. The lowest value at both deformation works was found when

the lowest value of radiation dose of 99 kGy was applied (Fig. 6). Also, the value of elastic part of indentation work η_{IT} which provides information about the relaxation of the indent created in LDPE was the smallest for non-irradiated LDPE.

Conclusion

Very interesting results were obtained for irradiation modified LDPE. When comparing the irradiated and non-irradiated LDPE it was apparent that the values of indentation hardness, elastic modulus considerably decreased, in some cases even by 31% at the irradiation dose of 33 kGy. Improvement of mechanical properties in micro and macro scale of radiated LDPE has a great significance also for industry. The modified LDPE shifts to the group of materials which have considerably better properties. Its micromechanical properties make LDPE ideal for a wide application in the areas where higher resistance to wear, creep are required. Commonly manufactured LDPE can hardly fulfill these criteria.

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References

- [1] G. Zamfirova, V. Gaydarov, T. Zaharescu, L. G. Silva, Microindentation study of Electron Beam Irradiated Polyamide Samples, *Chemicke Listy*, 104 (2010), 283-286.
- [2] A. Bolshakov and G.M. Pharr, Influences of pile-up on the measurement of mechanical properties by load and depth sensing indentation techniques, *Journal of Materials Research*. 13, (1998), 1049-1058.
- [3] W.C. Oliver, G.M. Pharr, Measurement of Hardness and Elastic Modulus by Instrumented Indentation, *Journal of Materials Research* 19 (1), (2004), 1564 – 1583.
- [4] D. Manas, M. Hribova, M. Manas, M. Ovsik, Stanek, Effect of Beta Irradiation on Morphology and Microhardness of Polypropylene Thin Layers, *Thin Solid Films* 530, (2013), 49-52.
- [5] Rajatendu Sengupta, S. Sabharwal, V. K. Tikku, Alok K. Somani, Tapan K. Chaki, Anil K. Bhowmick, Effect of ambient-temperature and high-temperature electron-beam radiation on the structural, thermal, mechanical, and dynamic mechanical properties of injection-molded polyamide-6,6, *Journal of applied polymer science*, 99 (4), (2006), 1633 -1644
- [6] M. Ovsik, D. Manas, M. Manas, M. Stanek, M. Hribova, K. Kocman, D. Samek, Irradiated Polypropylene Studied by Microhardness and WAXS, *Chemicke listy*, 106 (2012), 507-510.
- [7] A. Pusz, K. Michalik, Creep damage mechanisms in gas pipes made of high density polyethylene, 2009 *Archives of Materials Science and Engineering* 36 (2) , pp. 89-95